Chapter 55 - **CLUSTERING IN MACROMOLECULAR MEDIA**

1. INTRODUCTION

The clustering phenomenon is observed in many water-soluble macromolecular systems such as synthetic polymers and biological macromolecules. It has also been observed in mixtures of polar solvents as well. Clustering shows up as major aggregation in the sample on the micrometer length scale which produces a strong low-Q signal with SANS. It also shows up as a "slow" mode in Dynamic Light Scattering (DLS). A figure shows SANS data from a series of macromolecular systems. Note the low-Q clustering signal and the high-Q solvation signal. The solvation signal is either of a decreasing Lorenzian type shape or characterized by a correlation peak.

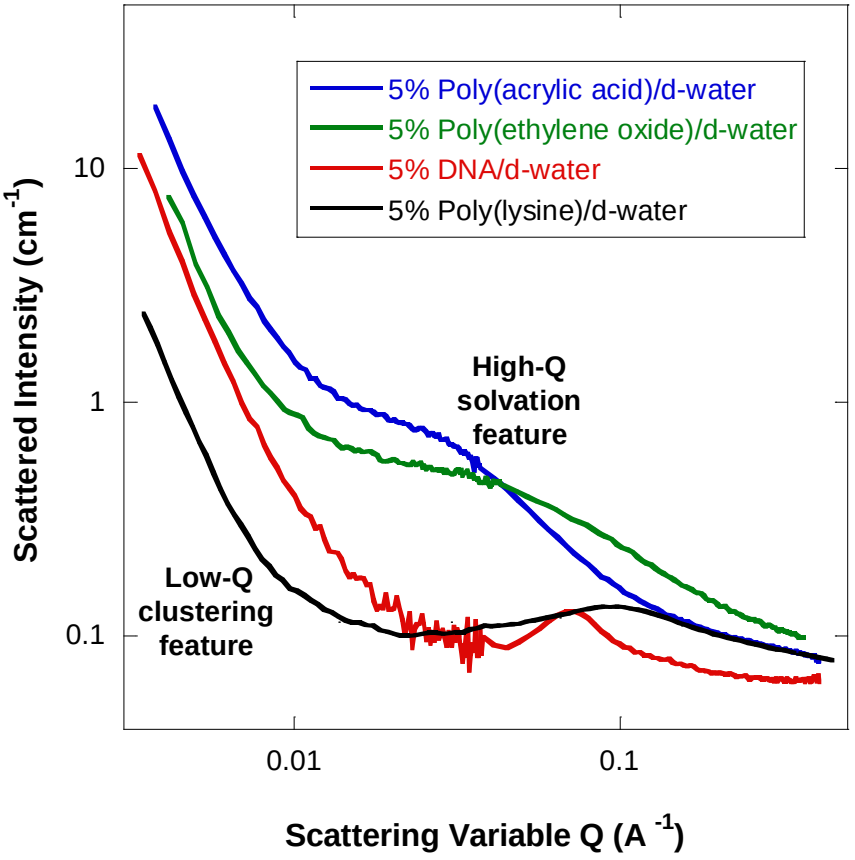

Figure 1: SANS data from two synthetic polymers and two biological macromolecules dissolved in deuterated water at ambient temperature (25 ^{o}C).

In order to understand possible cause(s) of clustering, the simplest water-soluble polymer, poly(ethylene oxide) or PEO is investigated in d-water.

2. CHAIN END CLUSTERING

A set of three PEO polymer chains (M_w=51,700, M_n=48,500 g/mol), were used in which chain ends were either both –OH, both –OCH_3 or –OH at one end and –OCH_3 at the other. Each of these three different polymers was dissolved in three different solvents, d-water (which is hydrophilic), d-benzene (which is hydrophobic), and d-methanol (which is amphiphilic) respectively. SANS measurements were taken from 4 % PEO in each one of these solvents and with one of the three differently end-capped polymers (Hammouda et al, 2004). Since PEO crystallizes in d-methanol at low temperature, SANS data are presented for 50 ^oC sample temperature for which crystallization has melted.

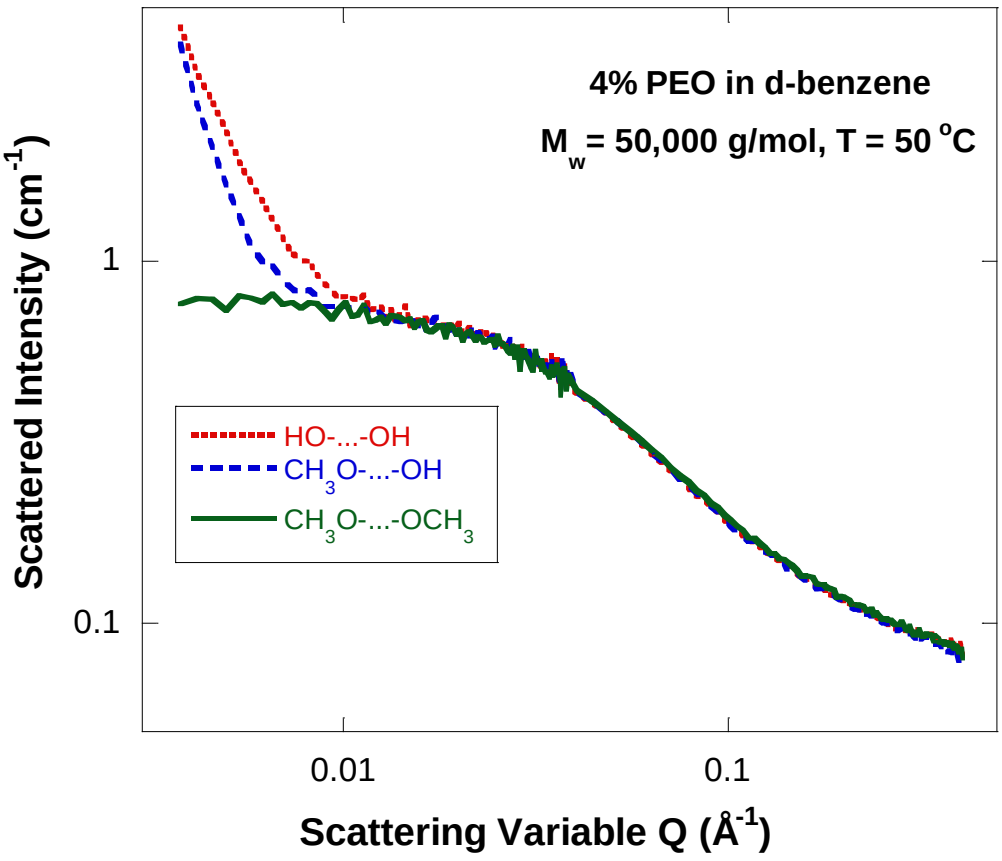

Figure 2: SANS intensity for the 4 % PEO/d-benzene case at 50 ^oC and for the three different chain end groups. Note that clusters disappear completely in the CH_3O-PEO-OCH_3 case.

In order to analyze the SANS data, the following empirical model for the scattering intensity is used:

$$I(Q) = \frac{A}{Q^n} + \frac{C}{1+(Q\xi)^m} + B. \qquad (1)$$

The first term describes Porod scattering from clusters and the second term describes scattering from dissolved polymer chains. This second term characterizes the polymer/solvent interactions and therefore the thermodynamics of mixing and phase separation. The two multiplicative factors A and C, the incoherent background B and the two Porod exponents n and m are used as fitting parameters. The clustering strength is defined as A/Q^n where Q = 0.004 $Å^{-1}$ is taken to be the lowest measured Q value for the used instrument configuration. The solvation strength is defined as parameter C.

The clustering strength (A/Q^n) is plotted for the three polymers in each of the three solvents. High clustering strength corresponds to networks (where both chain-ends stick to other chains), and low clustering strength corresponds to dissolved chains (no chain-end sticking). The intermediate case corresponds to branched structures (only one chain-end is tethered to other chains). As shown in the figure, the clustering strength is high when the end-group is solvent-phobic (such as for $–OCH_3$ in water or –OH in benzene) and low when the end-group dissolves well (such as for $–OCH_3$ in benzene or –OH in water). The clustering strength is small for both types of end-groups when using the amphiphilic methanol solvent.

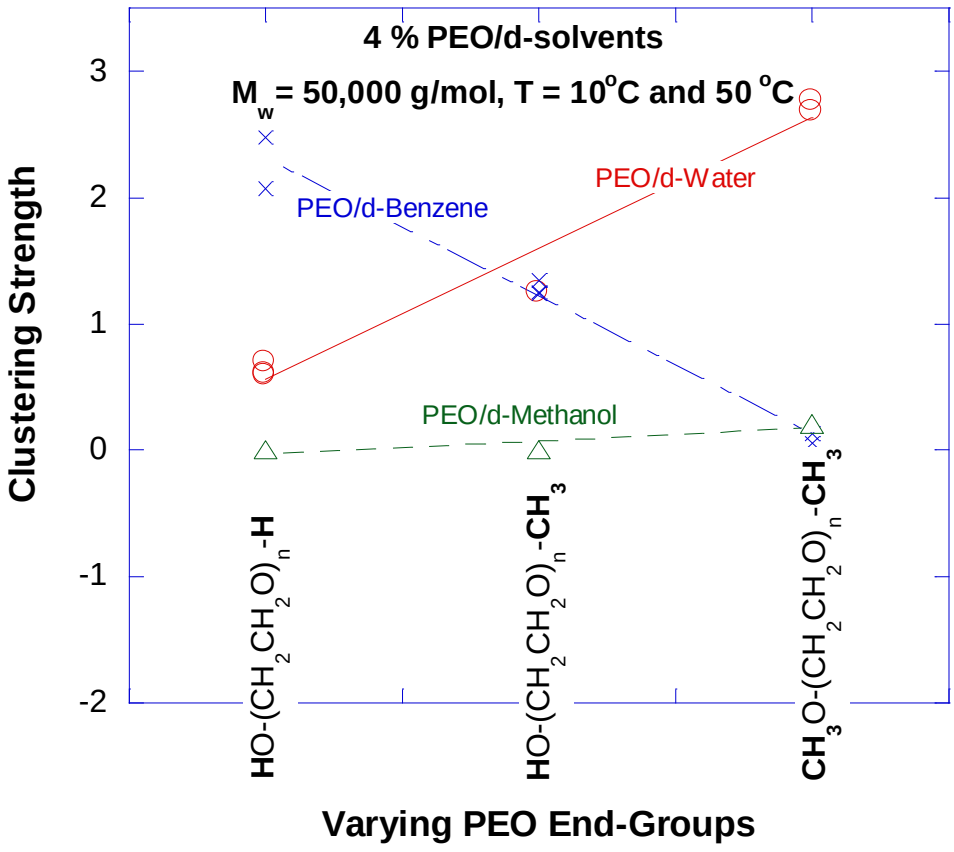

Figure 3: Variation of the clustering strength (obtained for the low-Q feature in the scattering) with PEO varying end-groups.

Given these SANS results, the cause of the chain-end form of clustering becomes clear. Clusters form when chain ends cannot stay dissolved because they are solvent phobic.

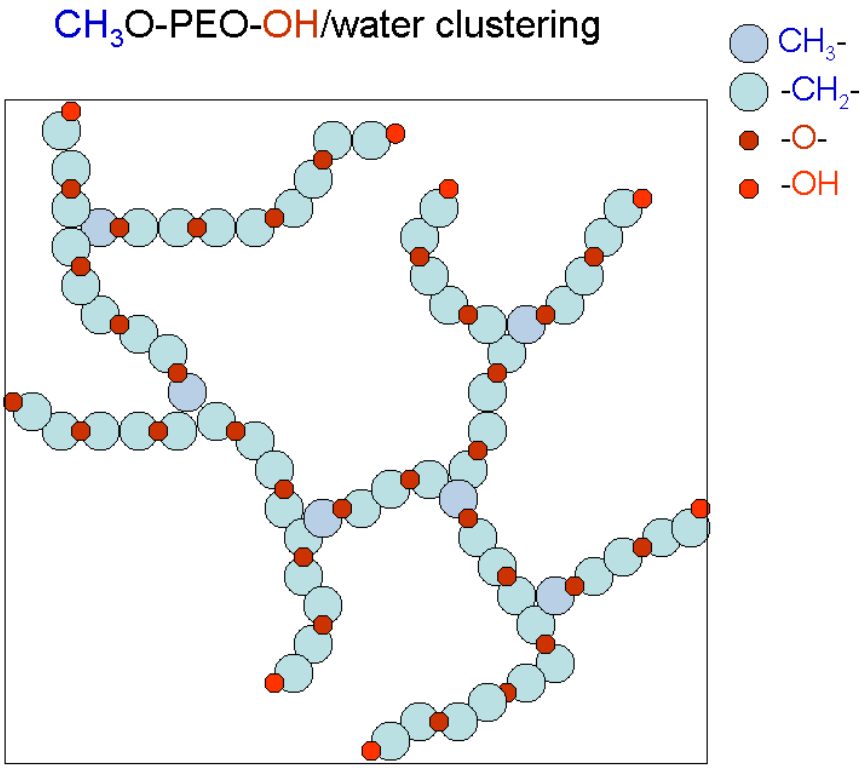

Figure 4 Schematic rendering (not to scale) of the PEO/d-water clusters in the case with different chain ends (-OCH_3 and –OH). The –OH end group stays dissolved in water whereas the –OCH_3 end group ends up sticking to other hydrophobic (CH_2CH_2) groups on the PEO chain. PEO chains become tethered at one end.

The anionic form of polymerization uses hydrophobic initiators which end up as chain ends. Hydrophobic chain ends are prevalent even for water-soluble polymers.

Another (more important) form of clustering is discussed next.

3. CLUSTERING DUE TO MONOMER STICKING INTERACTIONS

In order to assess the dominant form of clustering in macromolecular systems, a series of SANS measurements were performed from PEO/d-water solutions (Hammouda, 2009). The PEO molecular weights were M_w = 100 000 g/mol and M_n = 96 000 g/mol corresponding to a polydispersity index of M_w/M_n = 1.04. A set of seven samples were measured. These correspond to PEO volume fractions of 0.5 %, 1 %, 2 %, 3 %, 4 %, 5 %, and 10 %. The measured temperatures were 10 ºC, 30 ºC, 50 ºC, 70 ºC, and 90 ºC. A figure shows representative data from the 5 % PEO sample. The low-Q clustering feature and the high-Q solvation features are clearly observed.

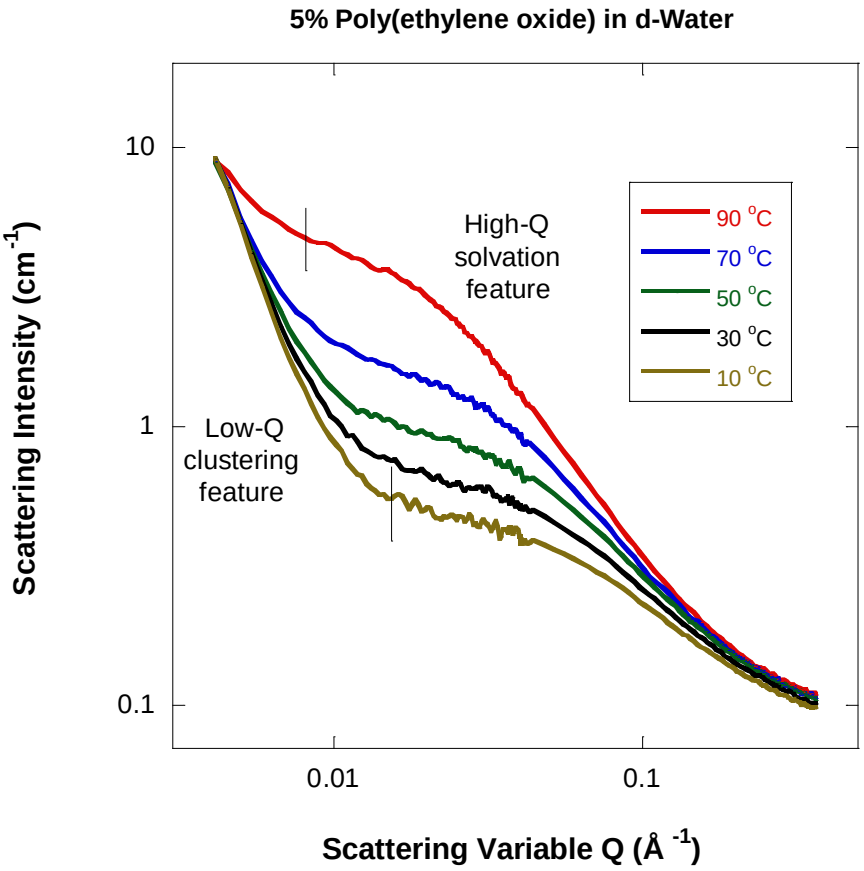

Figure 5: SANS from 5 % poly(ethylene oxide) in d-water for various temperatures. The low-Q clustering feature and the high-Q solvation feature can be clearly observed.

Another figure compares the low-Q clustering intensity A/Q^n and the high-Q solvation intensity C for the 5 % PEO/d-water sample in the measured temperature range. Clustering is seen to decrease while solvation increases with temperature. These two trends are opposite pointing to different driving forces for these two phenomena.

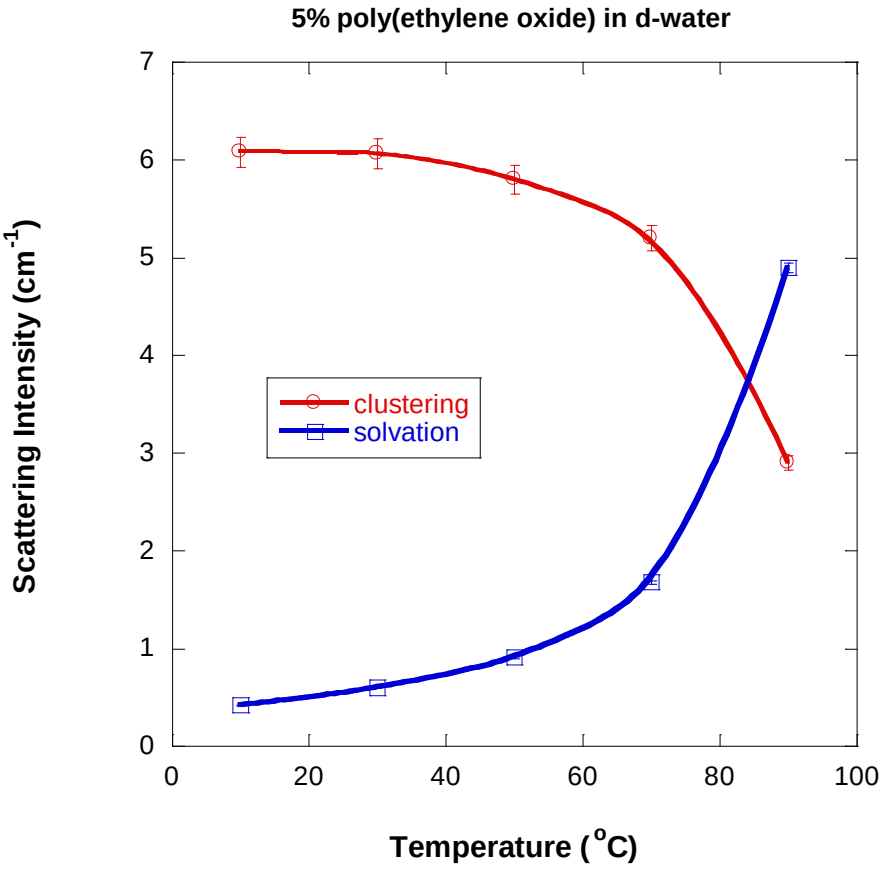

Figure 6: Variation of the clustering intensity A/Q^n and the solvation intensity C with increasing temperature. A low-Q value of 0.004 $Å^{-1}$ is used for the clustering intensity. Smooth curves have been included as a visual guide.

Increase of the solvation intensity with temperature characterizes a lower critical solution temperature (LCST) phase behavior in which phase separation occurs upon heating. Composition fluctuations increase when the phase boundary is approached leading to an increase in the scattering intensity (fitting parameter C). A plot of 1/C *vs* 1/T (where T is the absolute temperature) is characterized by a linear trend. Extrapolation to 1/C = 0 (solvation intensity "blows up") yields an estimate for the so-called spinodal temperature (98 °C for the 5 % PEO/d-water sample). Note that some other polymers in solution phase separate upon cooling and are characterized by an upper critical solution (UCST) instead.

In order to understand the low-Q clustering part, we consider the PEO monomer to be an alternating copolymer of an ethylene ($–CH_2CH_2–$) block and an oxygen (–O–) block and use the RPA model for regularly alternating block copolymers in solution. This is a ternary system containing the oxygen blocks (component 1), the ethylene blocks (component 2) and d-water (component 3). The ternary RPA equations are summarized here.

In the thermodynamic (Q = 0) limit, the scattering cross section (previously referred to as solvation intensity C) is given by:

$$\frac{d\Sigma}{d\Omega} \equiv C = \Delta\rho_1{}^2 S_{11} + \Delta\rho_2{}^2 S_{22} + 2\Delta\rho_1\Delta\rho_2 S_{12}. \qquad (7)$$

The relevant contrast factors are:

$$\Delta\rho_1{}^2 = (\rho_1 - \rho_3)^2 \qquad (8)$$
$$\Delta\rho_2{}^2 = (\rho_2 - \rho_3)^2.$$

The partial structure factors for the fully interacting mixture are given by:

$$S_{11} = \frac{S_{11}^0\left(1 + v_{21}S_{12}^0 + v_{22}S_{22}^0\right) - S_{12}^0\left(v_{21}S_{11}^0 + v_{22}S_{21}^0\right)}{\left(1 + v_{11}S_{11}^0 + v_{12}S_{21}^0\right)\left(1 + v_{21}S_{12}^0 + v_{22}S_{22}^0\right) - \left(v_{11}S_{12}^0 + v_{12}S_{22}^0\right)\left(v_{21}S_{11}^0 + v_{22}S_{21}^0\right)} \qquad (9)$$

$$S_{22} = \frac{S_{22}^0\left(1 + v_{12}S_{21}^0 + v_{11}S_{11}^0\right) - S_{21}^0\left(v_{12}S_{22}^0 + v_{11}S_{12}^0\right)}{\left(1 + v_{11}S_{11}^0 + v_{12}S_{21}^0\right)\left(1 + v_{21}S_{12}^0 + v_{22}S_{22}^0\right) - \left(v_{11}S_{12}^0 + v_{12}S_{22}^0\right)\left(v_{21}S_{11}^0 + v_{22}S_{21}^0\right)}$$

$$S_{12} = \frac{-S_{11}^0\left(v_{11}S_{12}^0 + v_{12}S_{22}^0\right) + S_{12}^0\left(1 + v_{11}S_{11}^0 + v_{12}S_{21}^0\right)}{\left(1 + v_{11}S_{11}^0 + v_{12}S_{21}^0\right)\left(1 + v_{21}S_{12}^0 + v_{22}S_{22}^0\right) - \left(v_{11}S_{12}^0 + v_{12}S_{22}^0\right)\left(v_{21}S_{11}^0 + v_{22}S_{21}^0\right)}$$

Excluded volume factors are defined in terms of the three Flory-Huggins interaction parameters (χ_{12}, χ_{13}, and χ_{23}) as:

$$v_{11} = \frac{1}{S_{33}^0} - 2\frac{\chi_{13}}{v_0} \qquad (10)$$
$$v_{22} = \frac{1}{S_{33}^0} - 2\frac{\chi_{23}}{v_0}$$
$$v_{12} = \frac{1}{S_{33}^0} + \frac{\chi_{12}}{v_0} - \frac{\chi_{13}}{v_0} - \frac{\chi_{23}}{v_0}.$$

The reference volume v_0 is expressed in each case as the square root of the product of the relevant volumes. The non-interacting scattering factors for this alternating copolymer solution are given by:

$$S_{11}^0 = n_1\phi_1 v_1 \qquad (11)$$
$$S_{22}^0 = n_2\phi_2 v_2$$
$$S_{12}^0 = \sqrt{n_1\phi_1 v_1 n_2\phi_2 v_2}$$

$$S_{33}^{0} = \phi_3 v_3 .$$

The volume fractions are related by $\phi_1+\phi_2+\phi_3 = 1$. The polymer volume fraction is $\phi_P = \phi_1+\phi_2$. The individual volume fractions are expressed as $\phi_1 = \phi_P \, n_1 v_1 / (n_1 v_1 + n_2 v_2)$ and $\phi_2 = \phi_P - \phi_1$.

The following sample information is used:

$n_1 = 2273$ (12)
$v_1 = 2.35*10^{-23}$ cm^3
$\rho_1 = 2.47*10^{-6}$ Å^{-2}
$n_2 = 2273$
$v_2 = 4.12*10^{-23}$ cm^3
$\rho_2 = -4.04*10^{-7}$ Å^{-2} .
$v_3 = 3.03*10^{-23}$ cm^3
$\rho_3 = 6.35*10^{-6}$ Å^{-2} .

Nonlinear least squares fits are performed using the ternary RPA model. SANS data files containing two columns (ϕ_P, C) for each temperature are used to back out the three Flory-Huggins interaction parameters χ_{12}, χ_{13}, and χ_2 for that temperature. In order to improve the fits, composition-dependent Flory-Huggins interaction parameters are considered. Linear best fit results of the temperature dependence are given by:

$$\chi_{12} = \left(-0.46 + \frac{27}{T}\right) + \left(-7.14 + \frac{3014}{T}\right)\phi_P \quad (13)$$

$$\chi_{13} = \left(0.59 - \frac{31}{T}\right) + \left(-3.51 - \frac{1477}{T}\right)\phi_P$$

$$\chi_{23} = \left(0.54 - \frac{50}{T}\right) + \left(11.25 - \frac{1425}{T}\right)\phi_P .$$

These results are summarized in the following figure.

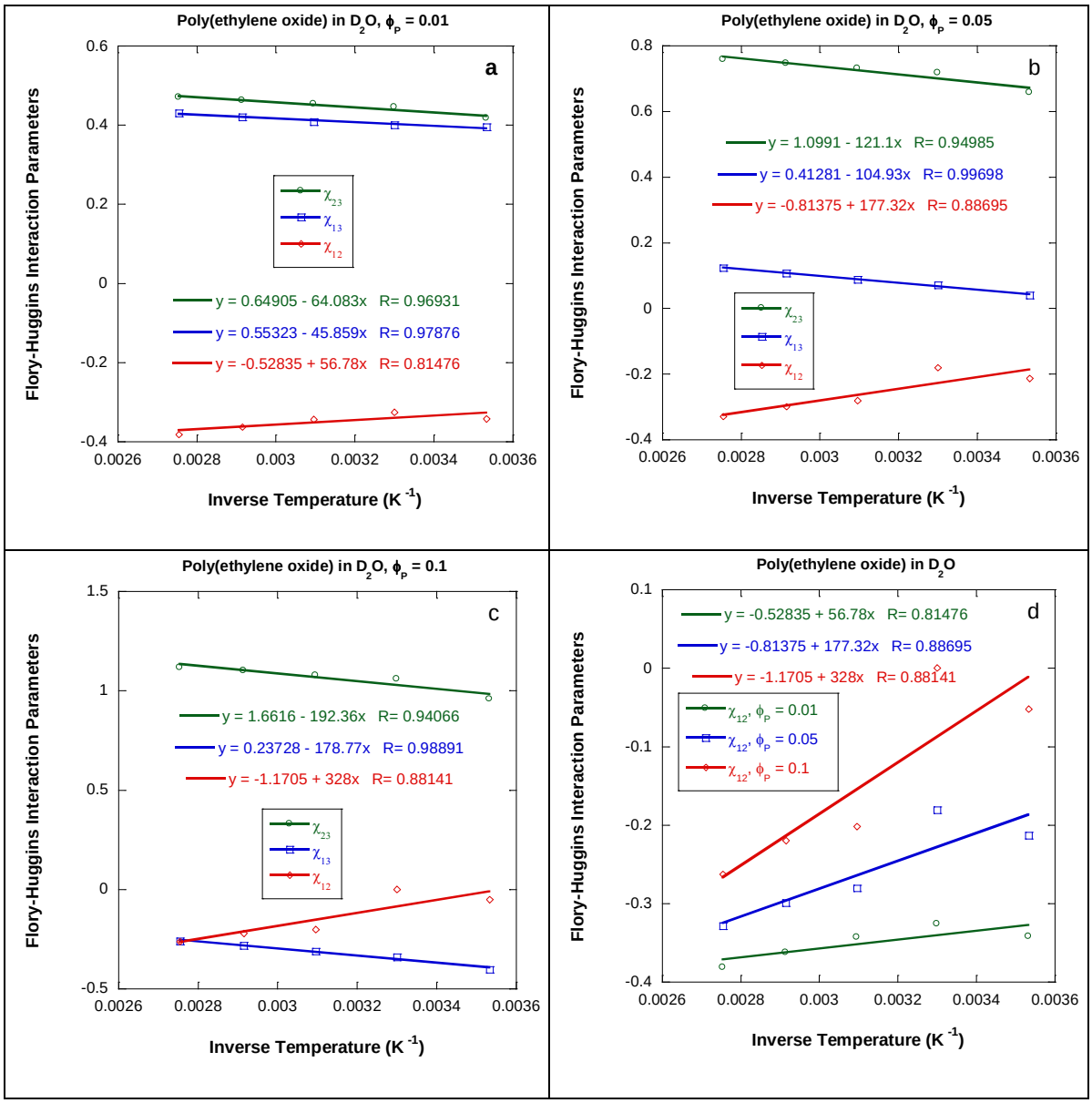

Figure 7: Variation of the Flory-Huggins interaction parameters between the three components: χ_{12} (oxygen/ethylene), χ_{13} (oxygen/d-water) and χ_{23} (ethylene/d-water). Case (a) corresponds to a PEO volume fraction of $\phi_P = 0.01$, case (b) corresponds to $\phi_P = 0.05$ and (c) case (c) corresponds to $\phi_P = 0.1$. Case (d) summarizes χ_{12} for increasing PEO fraction.

This figure shows that two of the Flory Huggins interaction parameters, χ_{13} (oxygen/d-water) and χ_{23} (ethylene/d-water) characterize an LCST phase behavior (phase separation upon heating) while the third one χ_{12} (oxygen/ethylene) characterizes a UCST phase behavior (phase separation upon cooling). The oxygen and ethylene groups, however, cannot phase separate since they form the PEO monomer (are covalently bound). This produces a "frustrated" system where the ethylene group is forced to remain next to the

backbone oxygen while it "prefers" to be close to another ethylene group. Ethylene groups remain dissolved but use any opportunity to stick to other ethylene groups on adjacent chains each time they get close enough. This produces physical crosslinks that form large clusters. Chain entanglements in semidilute and concentrated solutions produce favorable sites for close proximity of ethylene groups. The clustering process is kinetically driven.

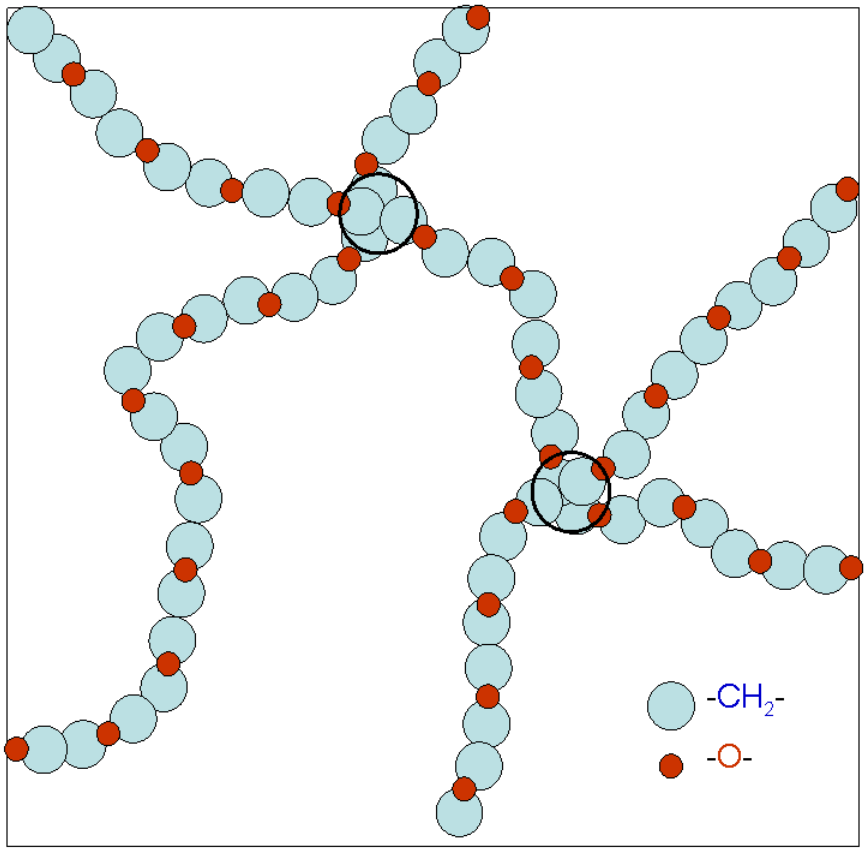

Figure 8: Schematic representation of dissolved PEO chains showing two clustering sites.

REFERENCES

B. Hammouda, D. Ho, and S. Kline, "Insight into Clustering in Poly(ethylene oxide) Solutions". Macromolecules 37, 6932-6937 (2004)

B. Hammouda, "The Mystery of Clustering in Macromolecular Media", Polymer 50, 5293-5297 (2009)

QUESTIONS

1. Define the various terms of the empirical SANS data analysis model given by

$$I(Q) = \frac{A}{Q^n} + \frac{C}{1+(Q\xi)^m} + B$$

2. What could produce a strong low-Q SANS signal?
3. What characterization methods could detect clustering in macromolecular media?
4. What are polar interactions? Are these the same type of interactions that produce clustering?

ANSWERS

1. In the empirical SANS data analysis model given by: $I(Q) = \frac{A}{Q^n} + \frac{C}{1+(Q\xi)^m} + B$, the first term A/Q^n represents the low-Q clustering feature and C represents the intermediate-Q solvation feature. A and C are scale factors, B is an incoherent background level, n and m are Porod exponents and ξ is a correlation length (length beyond which correlations die out).
2. A strong low-Q SANS signal could be due to crystallization, phase separation, inhomogeneities in the sample, aggregation or clustering.
3. Various characterization methods could detect clustering. These include microscopy (optical or electron microscopy), scattering methods (SANS, SAXS, DLS) and rheology (clustering produces shear thickening).
4. Polar interactions are between delocalized electrons in molecules. Polarity exists even in neutron molecules. Polarity is often represented by $\delta+$ or $\delta-$ on molecules. Same sign charges repel while opposite sign charges attract. Polar interactions are different from thermodynamic (hydrophobic, hydrophilic) interactions.